Excitonic Solar Cells: The Challenges of Efficiency and Durability

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Or.
"Convince an old skeptic like me that OPV has a future."

- Do not use anecdotal evidence.
  - e.g. Organic Light-Emitting Diodes, Liquid Crystal Displays, Conventional Photographs, Photocopiers, Car paint.
- No comparison with other thin-film technologies.
- From the viewpoint of basic science .

The questions to ask of an OPV device:

- How efficient is it?
- How long does it last?

- How big is it?
- How many can we make?
- How much do they cost?
- Can they be made sustainable?
- Do they contain toxic components?
- How much energy required to build?
- How do they work?

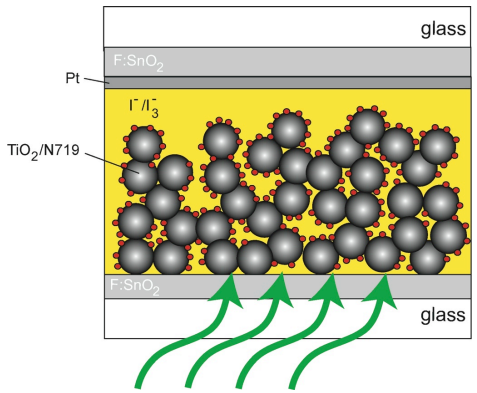
What is an OPV cell?

- Examples of Excitonic Solar Cells (XSC)
  - Dye-sensitized (Grätzel) solar cell (DSSC).
  - Two-layer, planar (Tang) solar cell.
  - Bulk heterojunction (Sariciftci and Heeger) solar cell.
  - Hybrids.
- Why ‘Excitonic’? Coupled/correlated electron-hole pairs.
  - Absorbed photon produces a neutral excitation, not free carriers. Therefore, a dissociation interface is required.

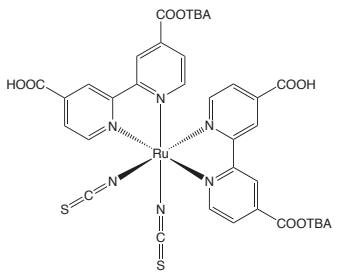
Excitonic Solar Cells

Dye-sensitised TiO_2 solar cell

O'Regan and Grätzel, *Nature*, **353**, 737 (1991)



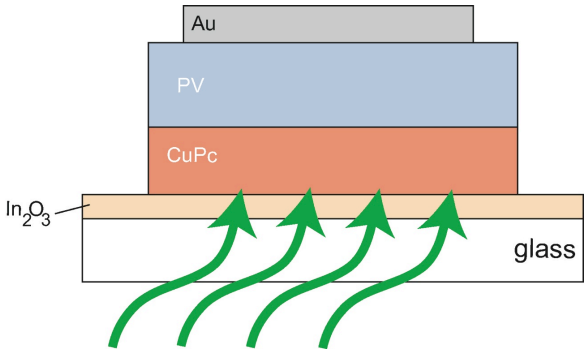
- Large titania surface area to increase absorption of adsorbed dye.
- Ultrafast and efficient electron injection from dye to titania.
- Redox couple to transport holes.



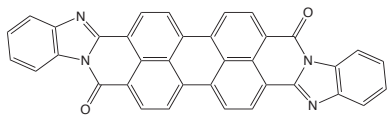
N719

Two-layer OPV cell

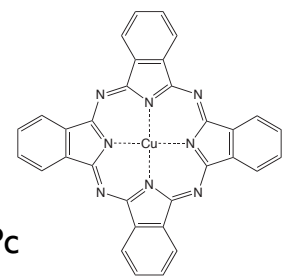
C.W.Tang, *APL*, **48(2)**, 183 (1986)



- Planar and simple.
- Vacuum deposited molecular films.
- Absorption by both layers.



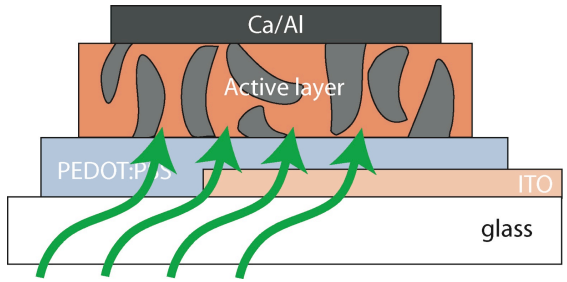
PV



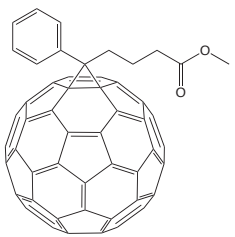
CuPc

Blended (bulk heterojunction) OPV cell

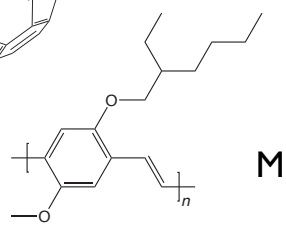
G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, *Science* **270**, 1789 (1995)



- Solution processible.
- Short exciton diffusion lengths.
- Ultrafast and efficient exciton dissociation.

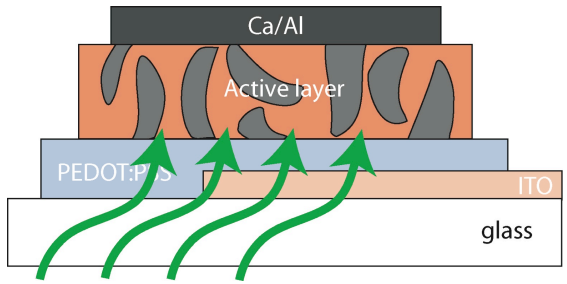


PCBM



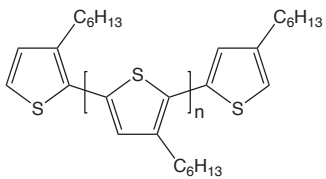
MEH-PPV

The Bulk Heterojunction (BH)

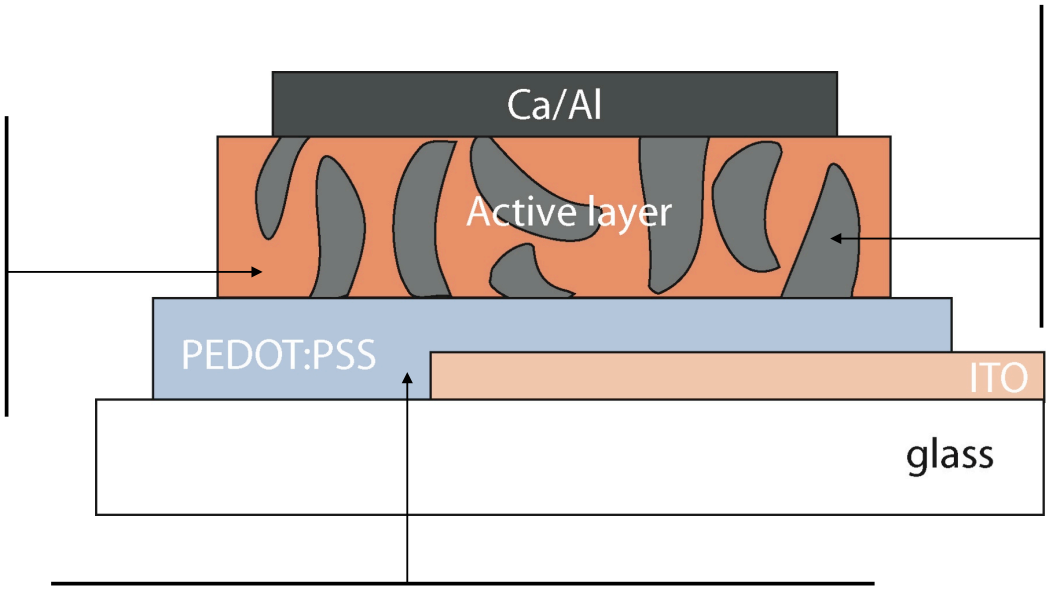


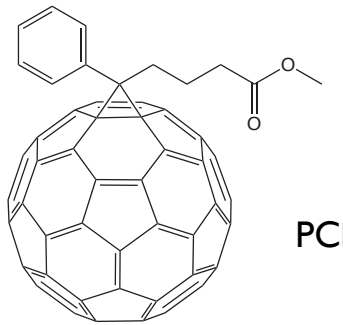
- Solution processible.
  - Both the PEDOT:PSS and Active layer can be deposited from solution. (e.g. Spin, Spray, Ultrasonic, Ink-jet, Doctor blade)
- Short exciton diffusion lengths.
  - Requires two components of the Active layer, the Donor and Acceptor, to phase separate and excitons not have to travel more than 10 nm.
- Ultrafast and efficient exciton dissociation.
  - Interface between Donor and Acceptor must efficiently dissociate exciton and inhibit recombination.

The Prototypical Poly(3-hexylthiophene): PCBM BH device

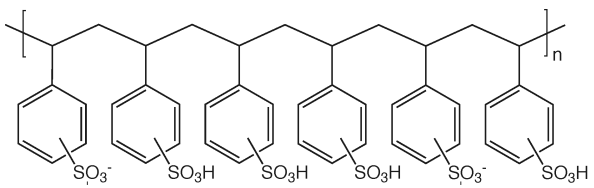


P3HT

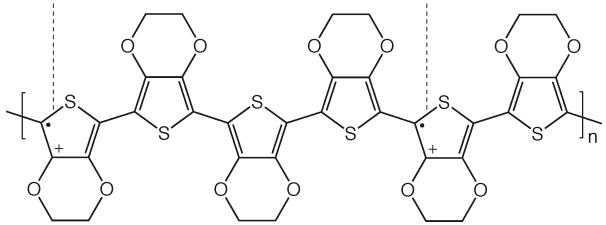




PCBM

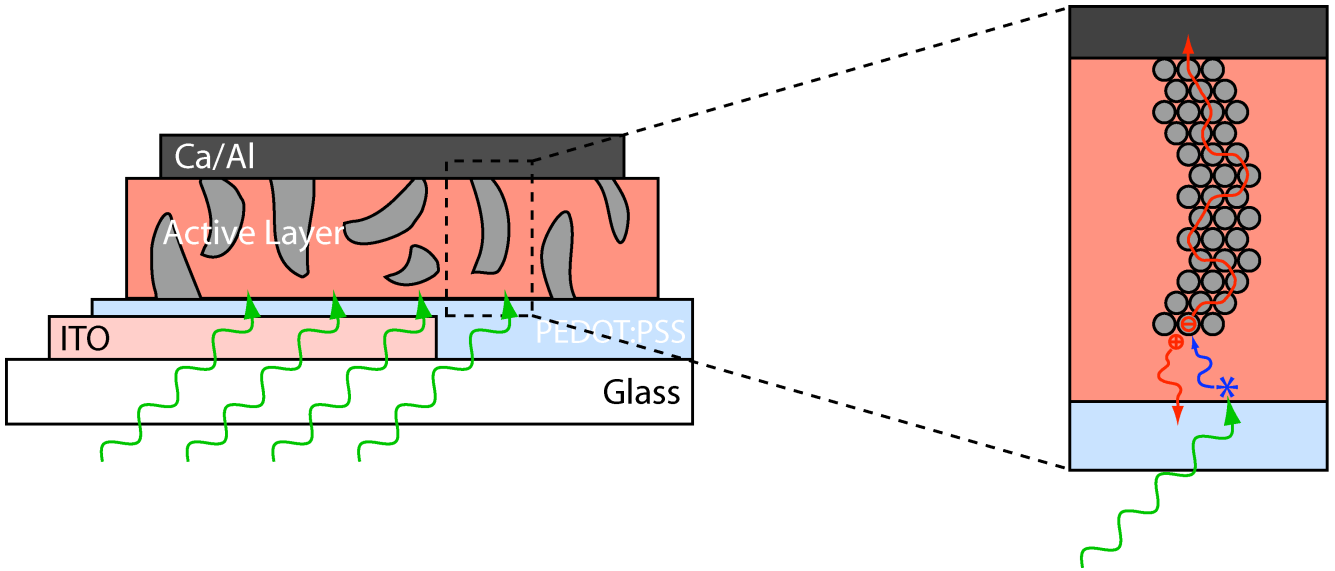


PSS



PEDOT

How it works



- P3HT absorbs photon.
- Exciton diffuses to interface.
- Exciton dissociates.
- Carriers diffuse, driven by chemical potential, to electrodes.
  - Electrons through PCBM network to cathode.
  - Holes through P3HT phase to anode.

Why P3HT and PCBM?

- P3HT absorbs further to the red, with optical bandgap at < 2 eV.
  - But Short Exciton lifetime, τ, ~ 300 - 500 ps.
- Exciton migrates to interface
  - But Diffusion length < 10 nm. Hence blend.
- Exciton dissociates to electron and hole at interface with PCBM.
  - Ultrafast, 100% yield, minimal recombination.
- Carrier recombination is minimal.
  - Why?
- Holes transport through P3HT.
  - Hole mobility, μ_h, > 10^{-3} cm^2/Vs
- Electrons transport (hopping) through PCBM.
  - Electron mobility, μ_e, > 10^{-3} cm^2/Vs

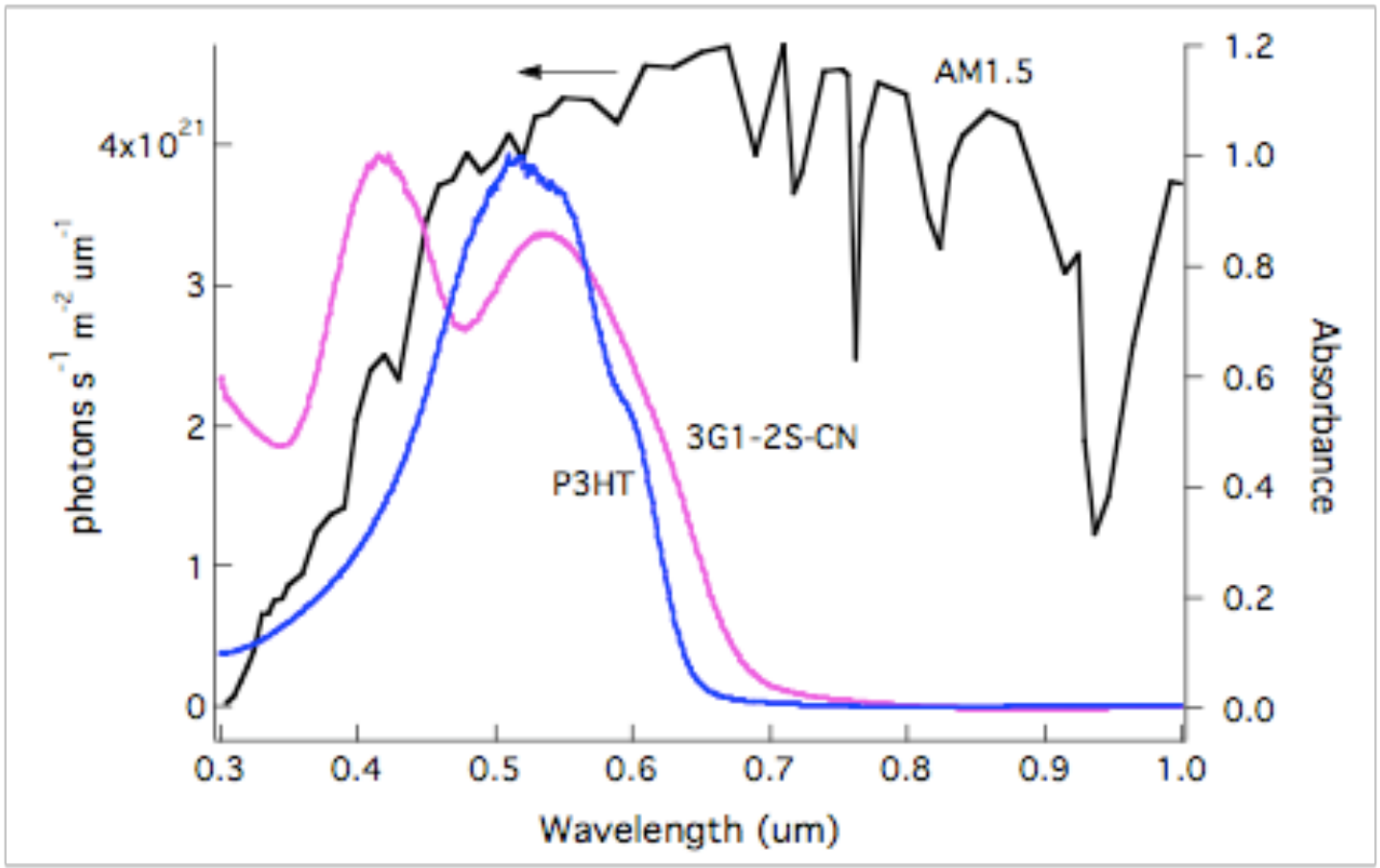
- Summary:
  - P3HT is a good absorber, it is ordered and therefore exhibits good hole (and possibly exciton) mobility.
  - PCBM forms an ideal donor-acceptor interface with P3HT.

Champion P3HT:PCBM devices

	Now	Realistic	How?
V_{oc} (V)	0.62	0.65	
J_{sc} (mA/cm^2)	10	14	Increase absorption (OD 2), reduce recombination
FF (%)	67	75	Reduce series resistance from 50 to 15 Ω
Efficiency (%)	(4.2)*	6.8	

*Yang Yang UCLA

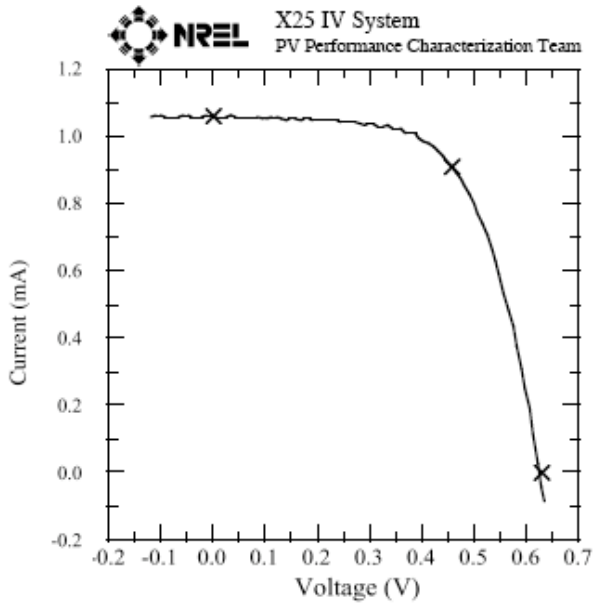
Red absorber



How Stable?

Device ID: 070407mor_A
Jul 05, 2007 11:01
Spectrum: AM1.5 Global

Device Temperature: 25.0 ± 1.0 °C
Device Area: 0.112 cm^2
Irradiance: 1000.0 W/m^2

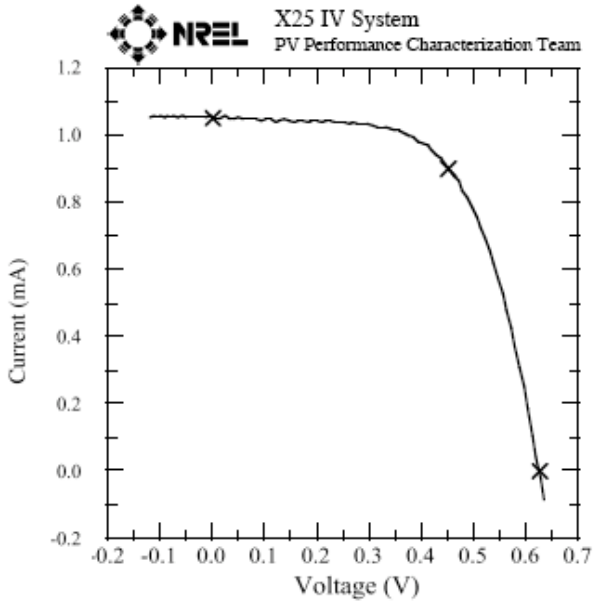


V_{oc} = 0.6268 V
I_{sc} = 1.0578 mA
J_{sc} = 9.411 mA/cm^2
Fill Factor = 62.50 %

I_{max} = 0.90810 mA
V_{max} = 0.4563 V
P_{max} = 0.41438 mW
Efficiency = 3.69 %

Device ID: 070407mor_F
Jul 05, 2007 11:45
Spectrum: AM1.5 Global

Device Temperature: 25.0 ± 1.0 °C
Device Area: 0.111 cm^2
Irradiance: 1000.0 W/m^2



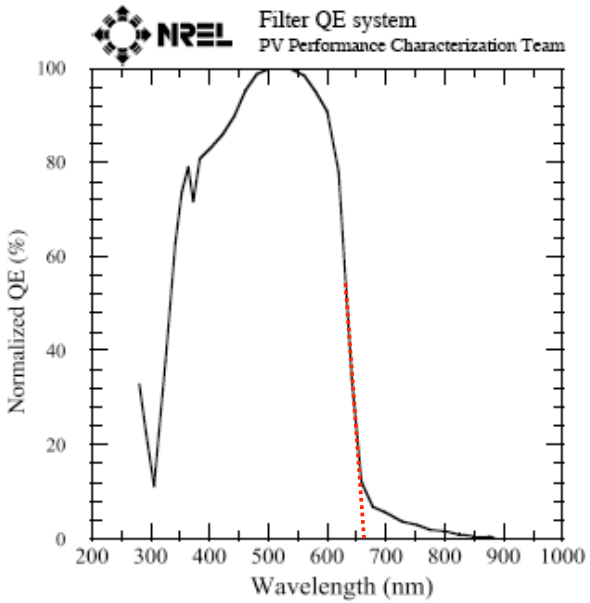
V_{oc} = 0.6257 V
I_{sc} = 1.0499 mA
J_{sc} = 9.450 mA/cm^2
Fill Factor = 61.78 %

I_{max} = 0.90007 mA
V_{max} = 0.4511 V
P_{max} = 0.40596 mW
Efficiency = 3.65 %

IPCE

Device ID: 070407mor_A
Jul 05, 2007 12:10

Device Temperature: NaN ± NaN°C
Device Area: 0.150 cm^2

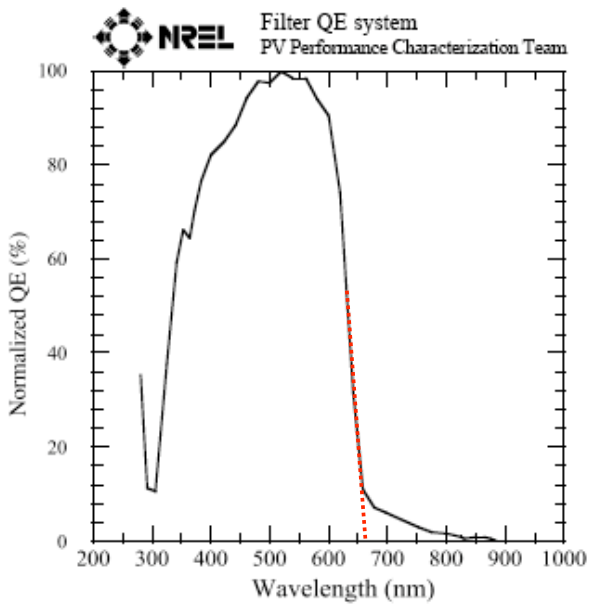


Voltage bias: 0.000E+0 V
Light bias current: 0.2 mA
Light Biased area: 0.15 cm^2
Light bias current density: 1 mA/cm^2

Cal: FQE pyro - ref cell cal 070705-1139

Device ID: 070407mor_A
Jul 05, 2007 12:48

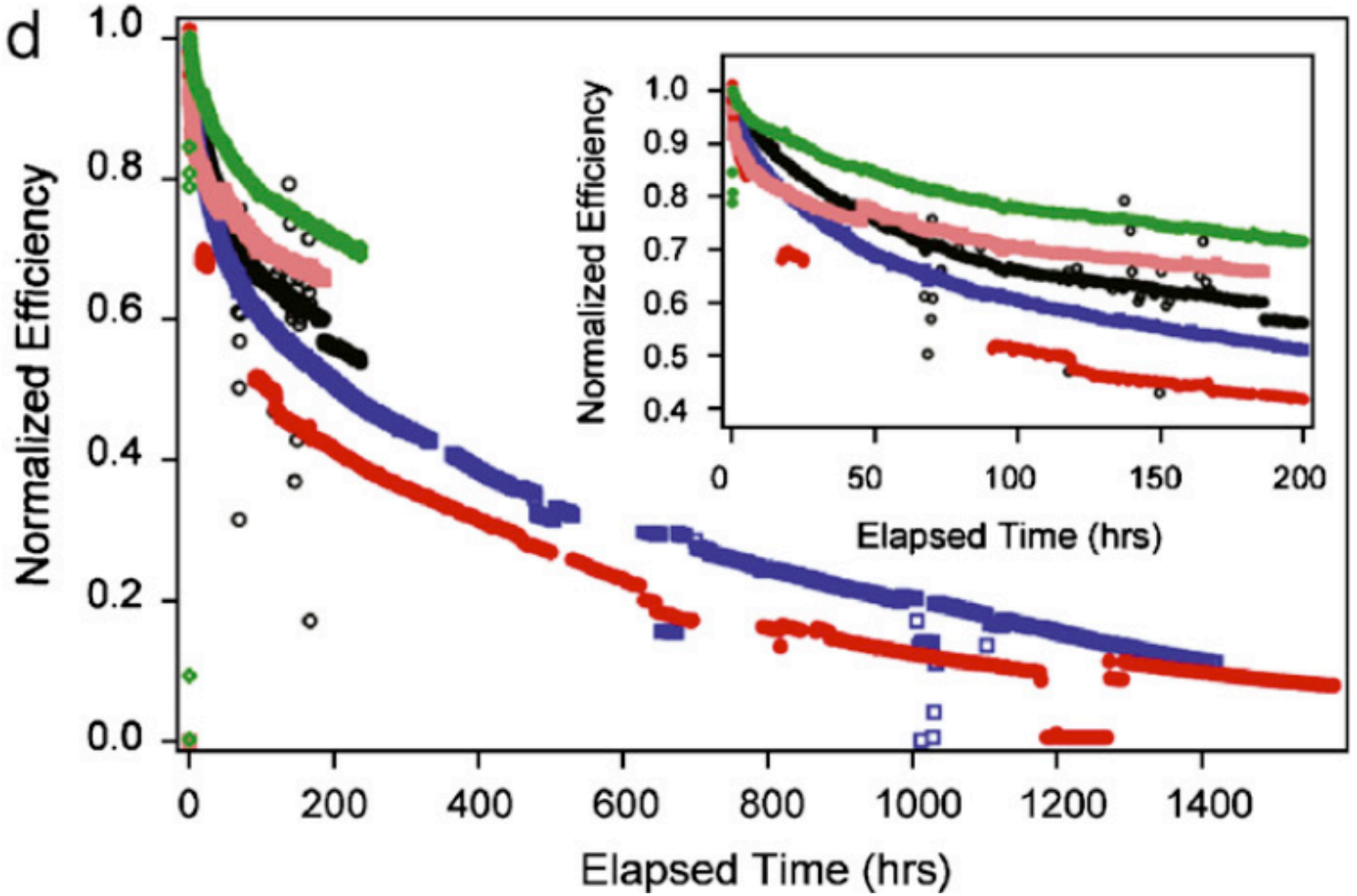
Device Temperature: NaN ± NaN°C
Device Area: 0.150 cm^2



Voltage bias: 0.000E+0 V
Light bias current: 1.0 mA
Light Biased area: 0.11 cm^2
Light bias current density: 9 mA/cm^2

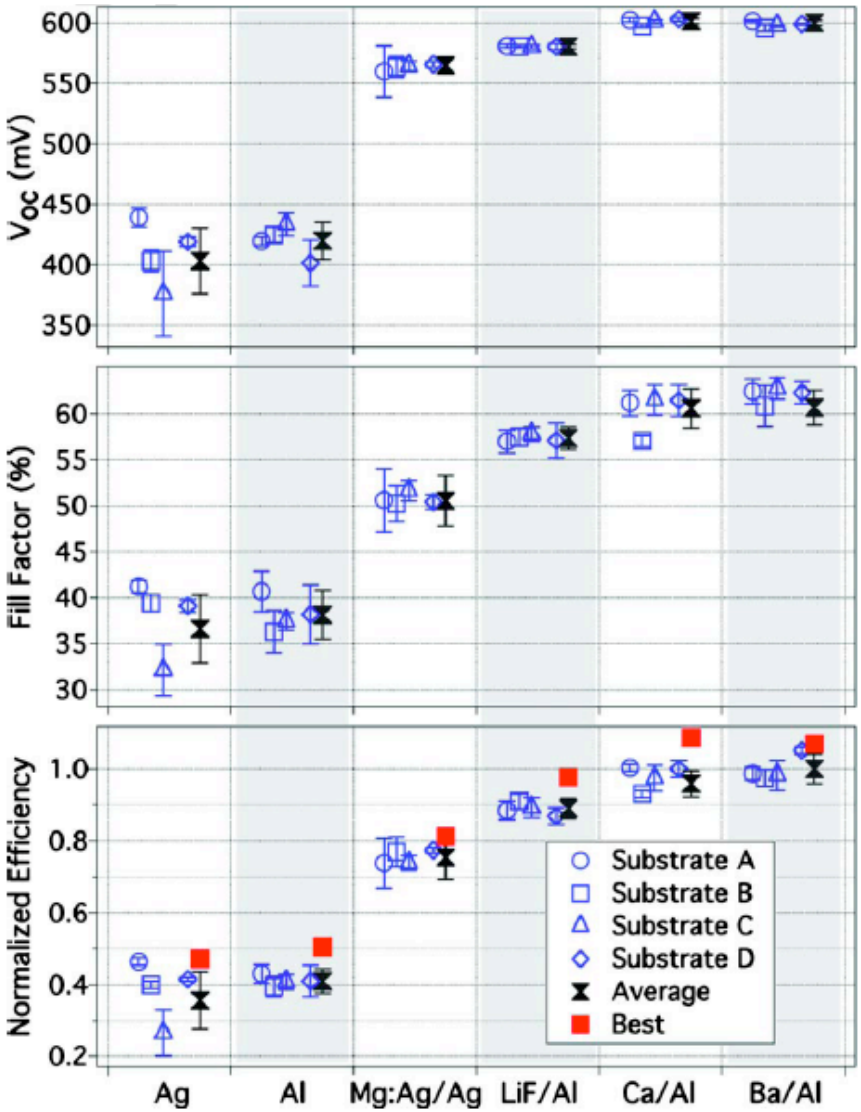
Cal: FQE pyro - ref cell cal 070705-1139

How Stable?



Look for 'report from Degradation Summit'. Defining standards for OPV

Top contact and reproducibilty



Source of instability?

Extrinsic effects

- Oxygen, Water and UV light.
  - Reduction
  - Sensitization
- Contacts
  - Acidity of PSS
  - Delamination
  - Reducing metals

Intrinsic effects

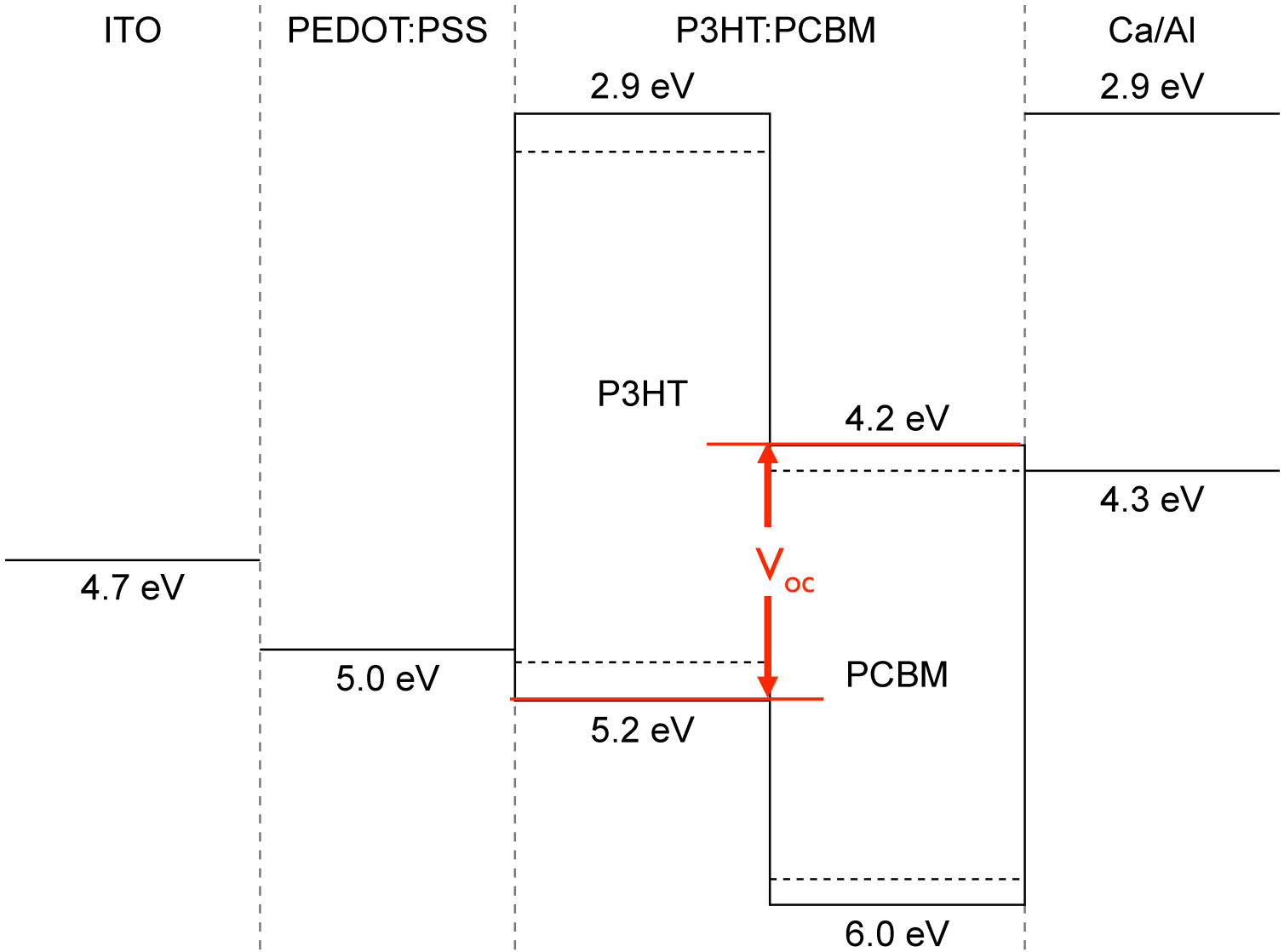
- Oxidising species
  - $Polaron^{+}$
- Reducing species
  - $Polaron^{-}$, $PCBM^{-}$
- Adventious dopants!
- Thermal
  - Internal conversion

Champion devices

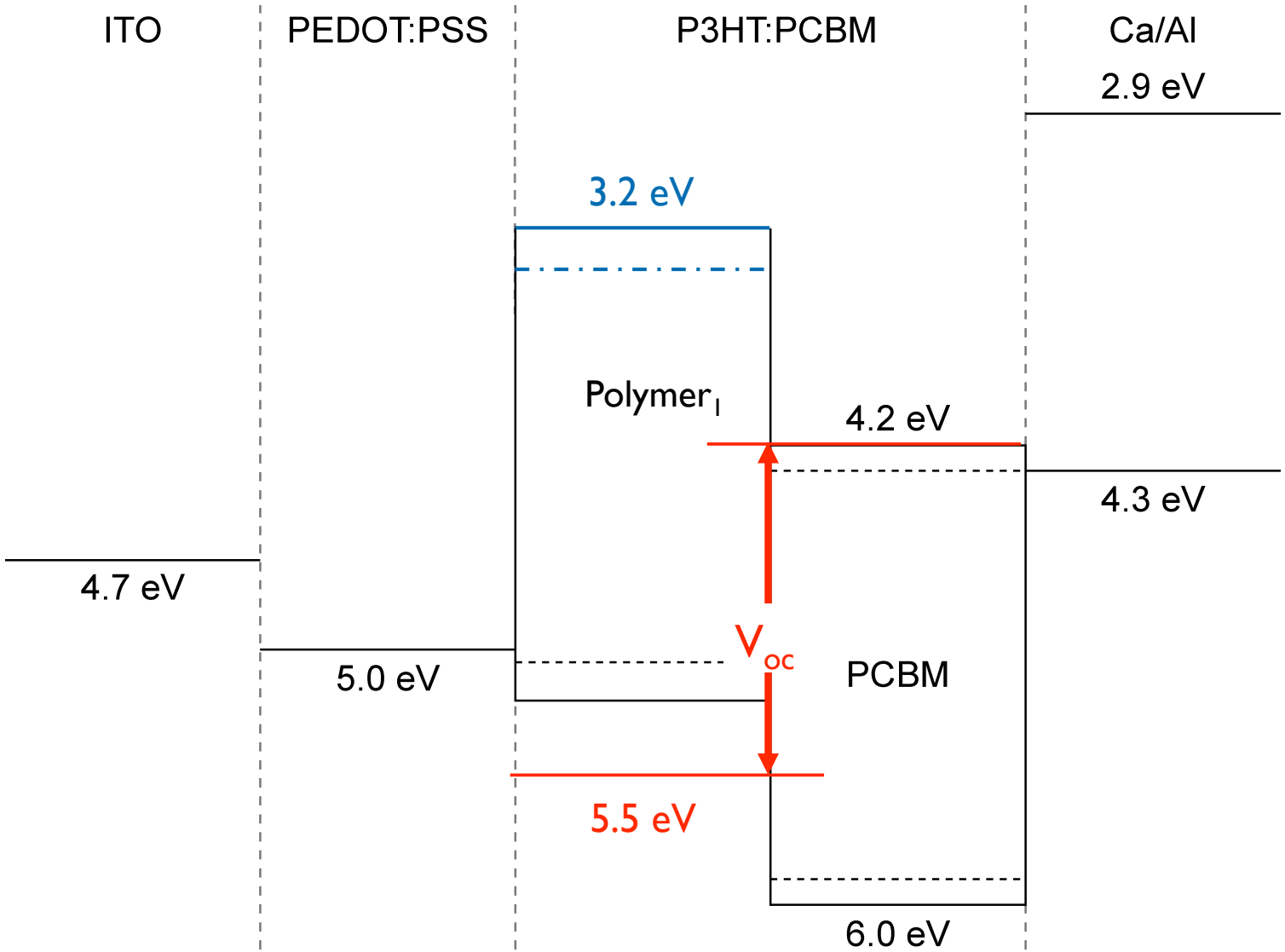
	Now	Realistic	Plan*	How?
V_{oc} (V)	0.62	0.65	1.1	Lower LUMO (and HOMO)
J_{sc} (mA/cm^2)	10	14	25	Shift absorption to red
FF (%)	67	75	80	Improve transparent electrode
Efficiency (%)	(4.2)	6.8	22	Larger carrier mobilities

* Sean Shaheen. Department of Physics, DU and NREL.

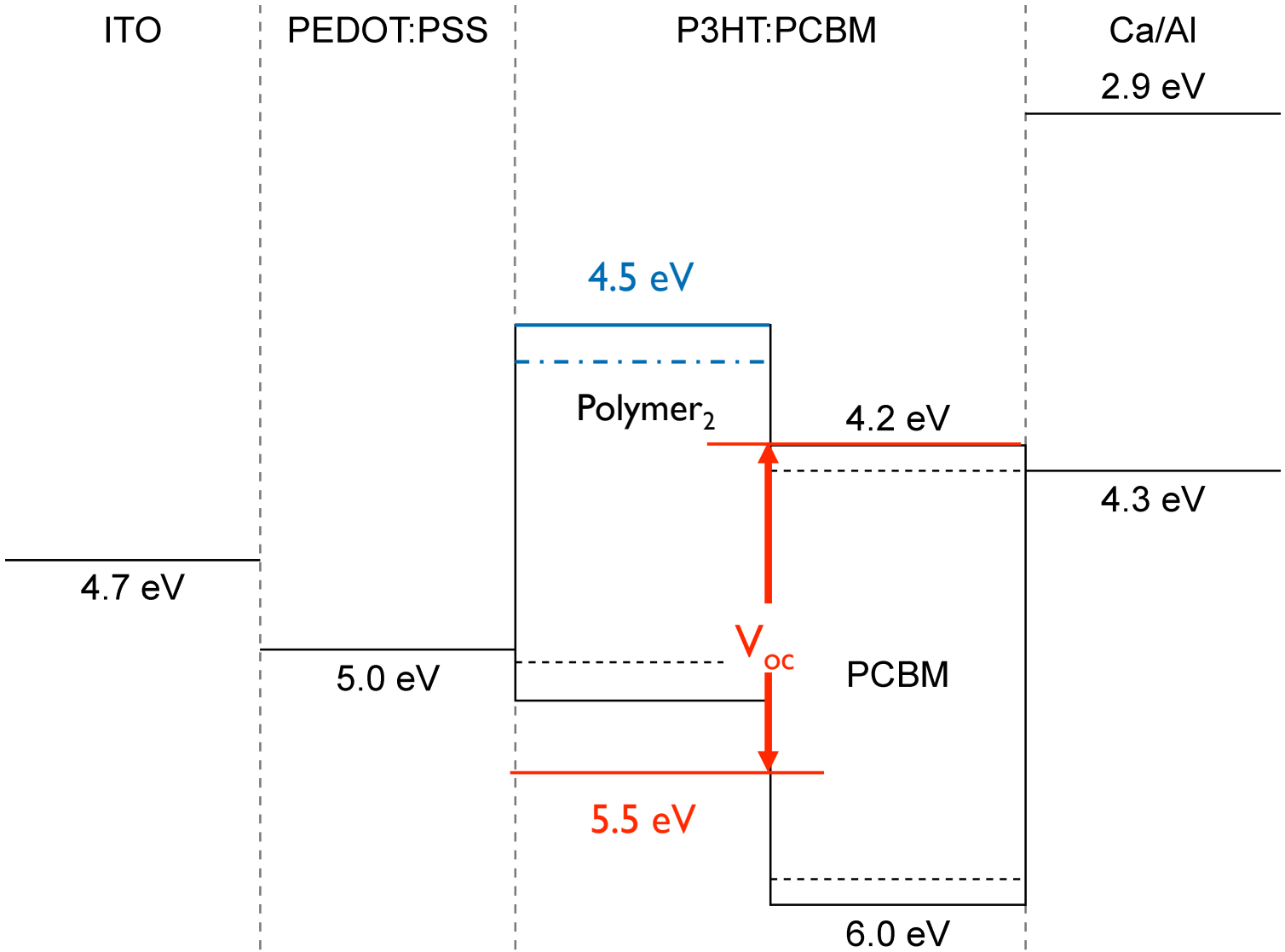
So this is what it looks like?



Improve stability



Improve stability and absorb more red

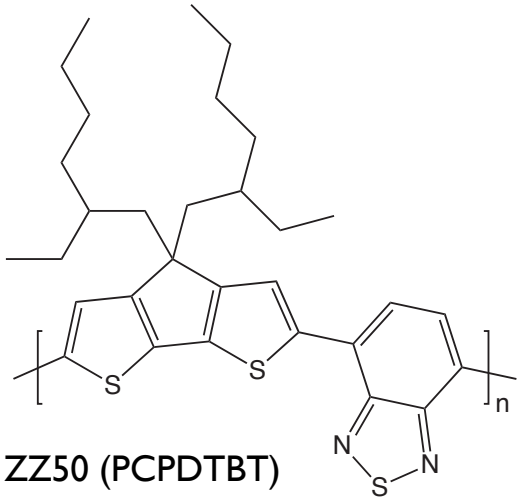


But. Everything else remains the same?

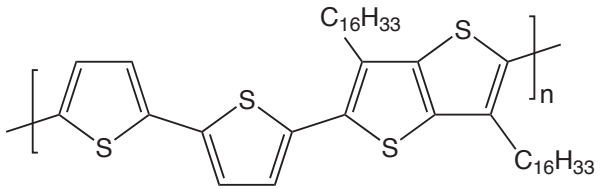
- Exciton binding energy
- Still exciton dissociation?
- Still minimal recombination (Marcus theory)?
- Same morphology!
  - Mobilities same?

- Any successes?

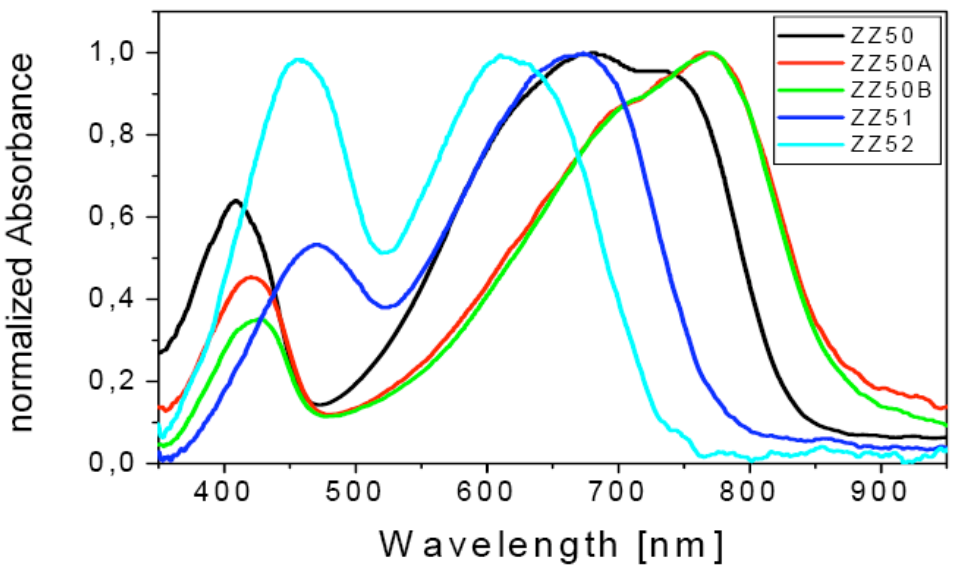
Changing the polymer…..

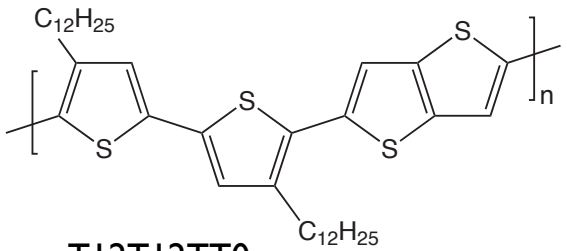


ZZ50 (PCPDTBT)



T0T0TT16



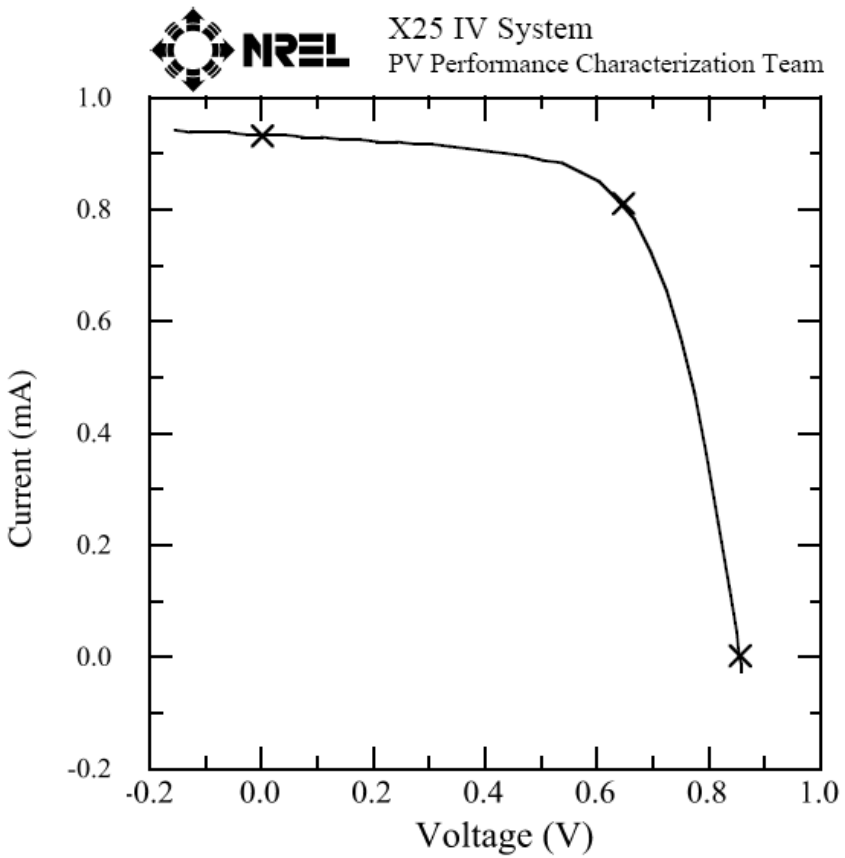


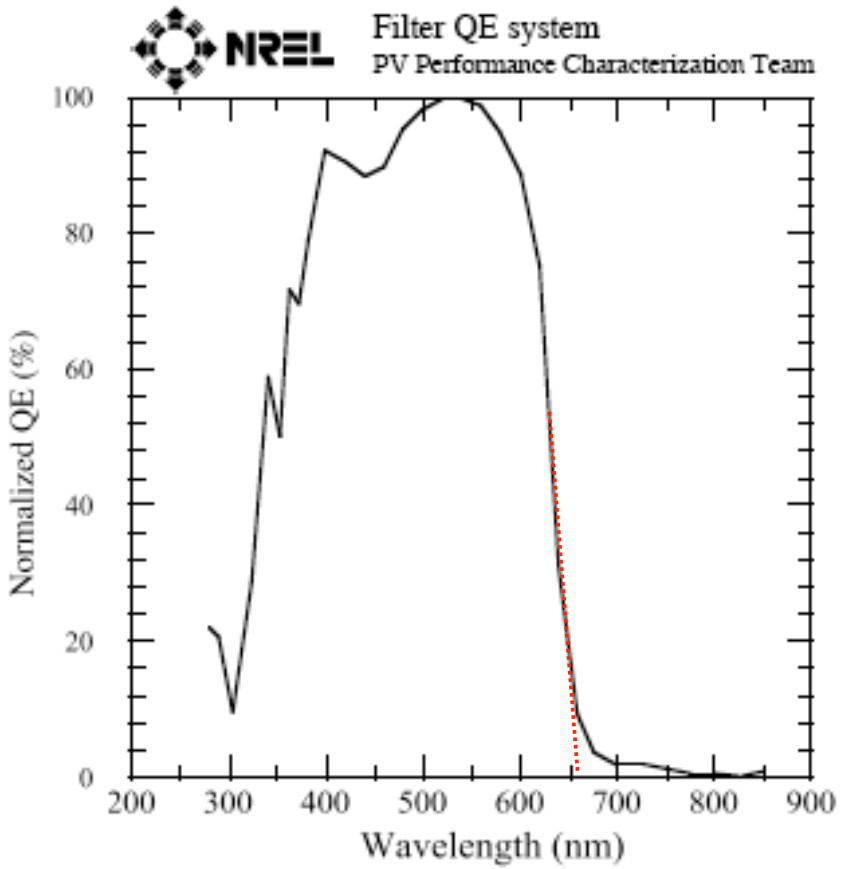
T12T12TT0

Plextronics - Plexcore® PV NREL-Certified Performance

Jul 17, 2007 11:50
Spectrum: AM1.5-G (IEC 60904)

Device Area: 0.096 cm^2
Irradiance: 1000.0 W/m^2

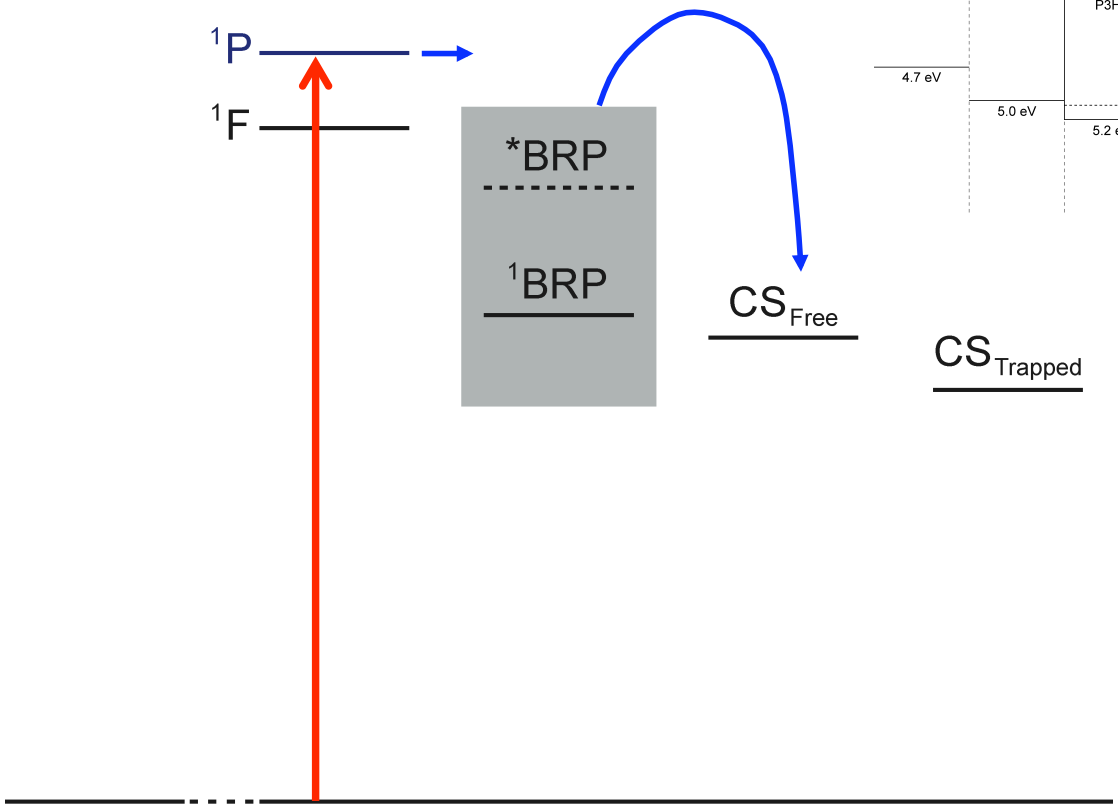


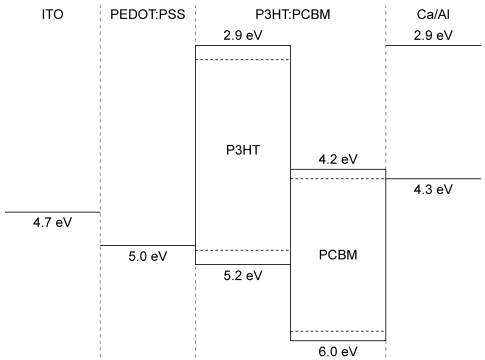


V_{oc} = 0.8563 V
I_{sc} = 0.93132 mA
J_{sc} = 9.7013 mA/cm^2
Fill Factor = 65.26 %

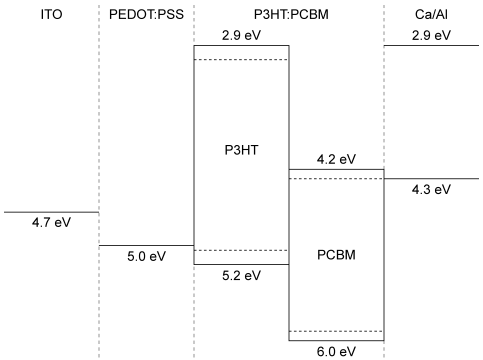
I_{max} = 0.80664 mA
V_{max} = 0.6452 V
P_{max} = 0.52048 mW
Efficiency = 5.42 %

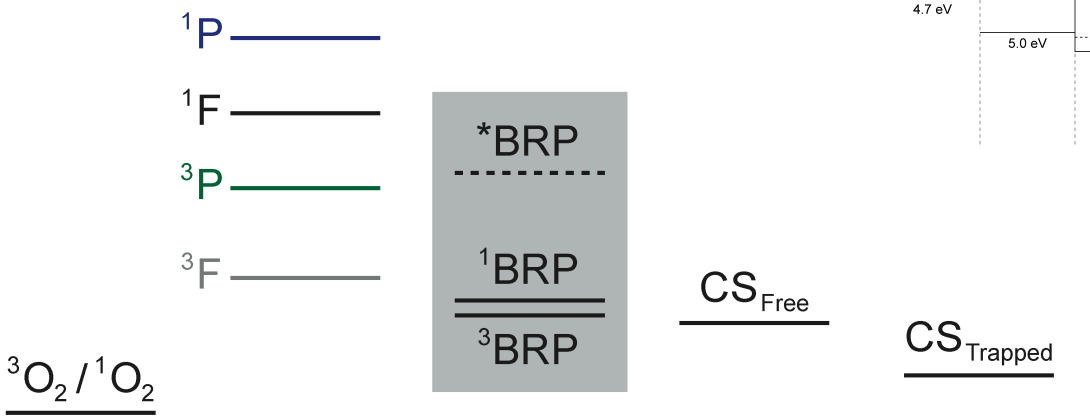
Introducing States





Triplets!


ITO
PEDOT:PSS
P3HT:PCBM
Ca/Al
2.9 eV
2.9 eV
P3HT
4.2 eV
4.3 eV
4.7 eV
5.0 eV
PCBM
5.2 eV
6.0 eV

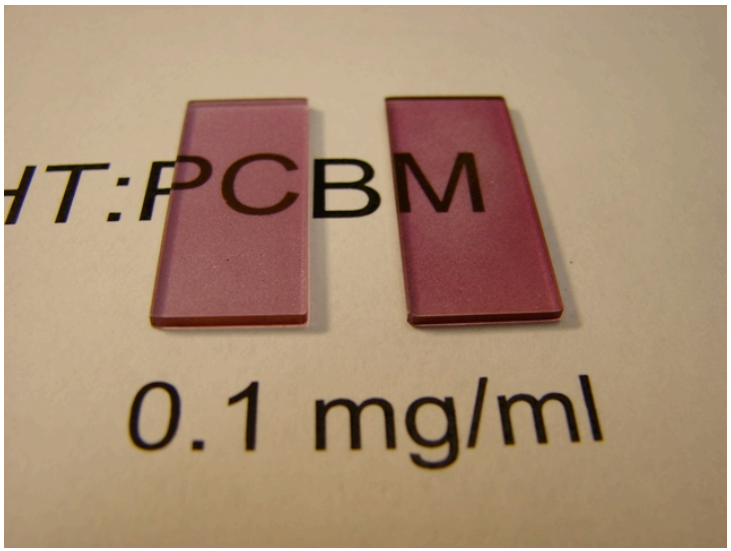

^1P
^1F
^3P
^3F
*BRP
^1BRP
^3BRP
CS_{Free}
$CS_{Trapped}$
$^3O_2 / ^1O_2$

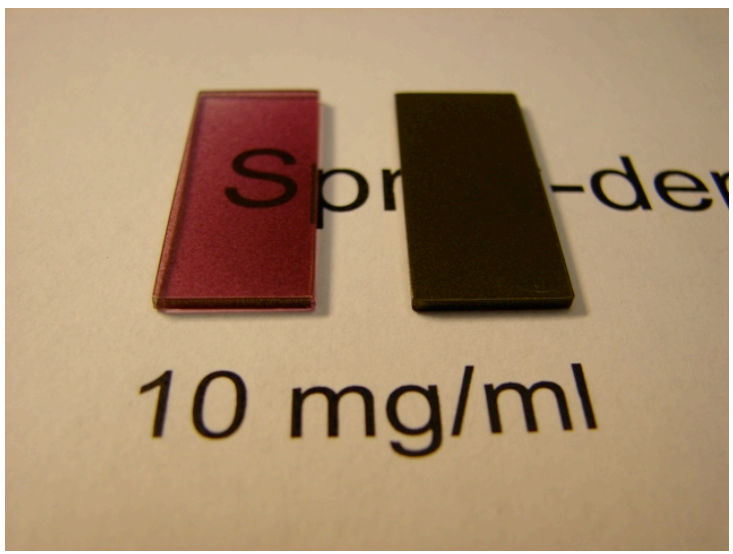
Biased by the skeptics:

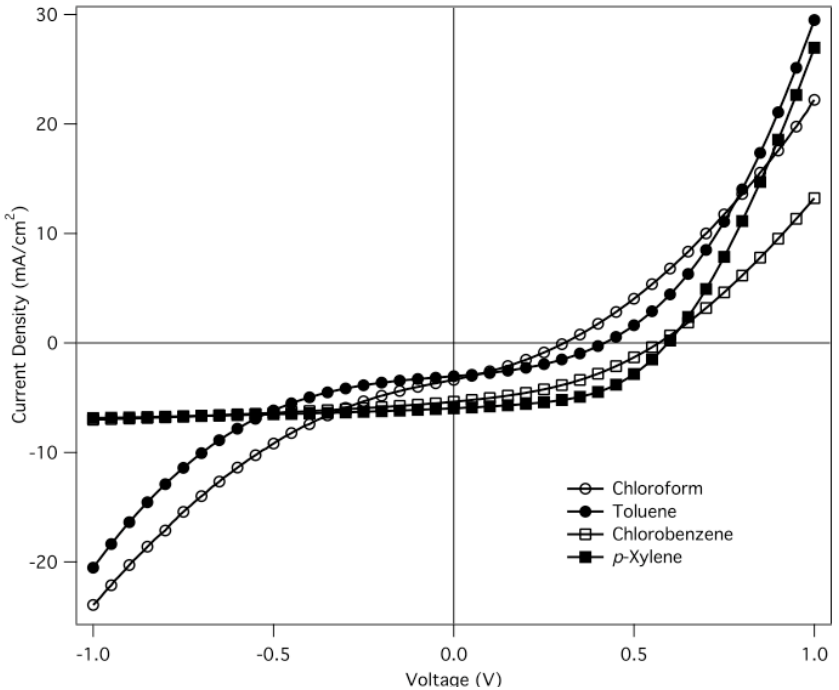
- How efficient is it?
- How long does it last?

- How big is it?
- How many can we make?
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- How do they work?

Spray-deposited devices



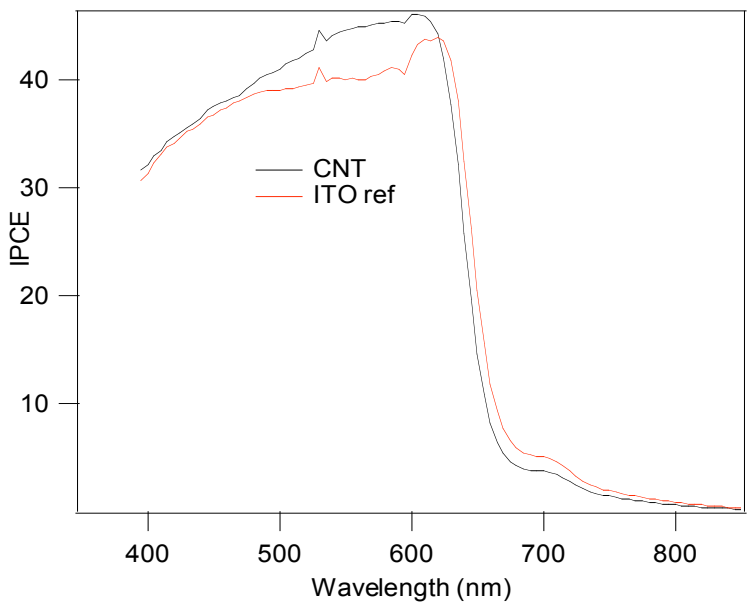


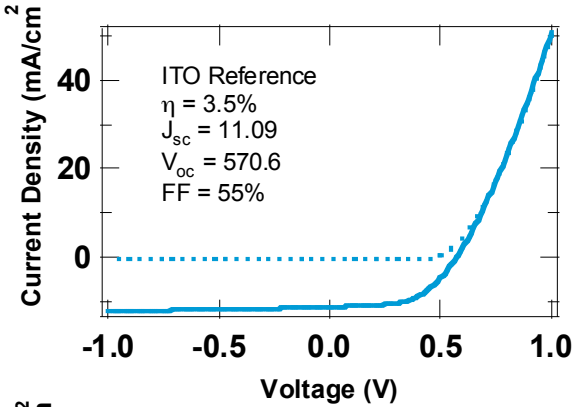


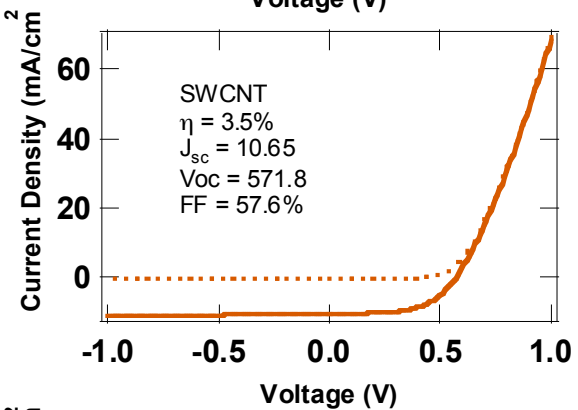


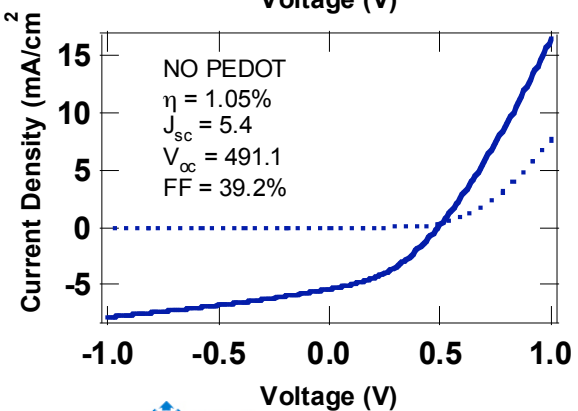
Devices on NREL doped-SWNT Networks

- Ultrasonic spray deposition
- Several ~ 3% devices
- Thick active layers - spun at 200 rpm
- Reducing electrode roughness is key
- PEDOT can be eliminated

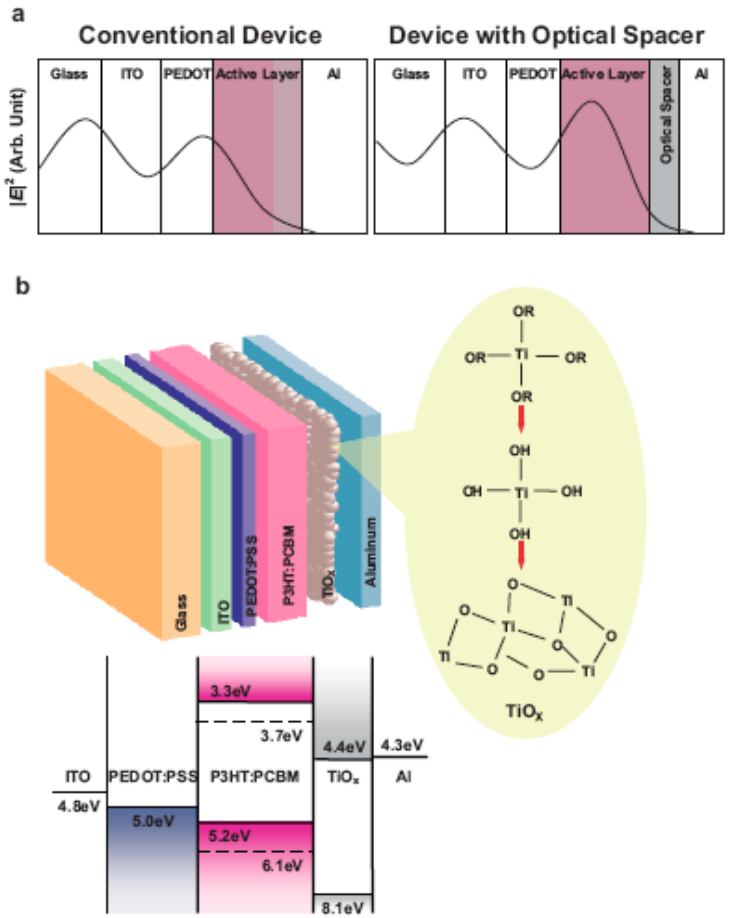


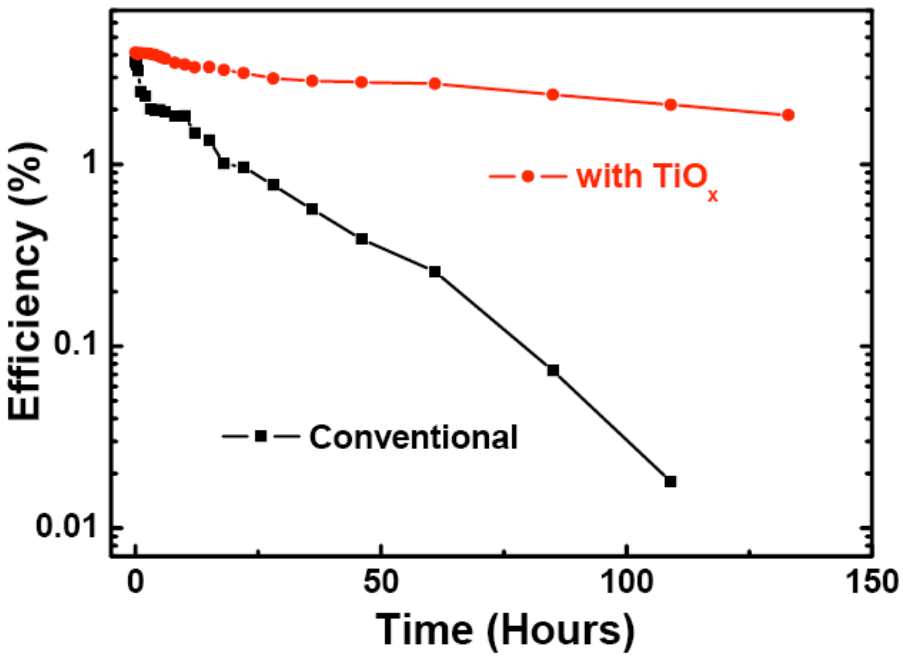






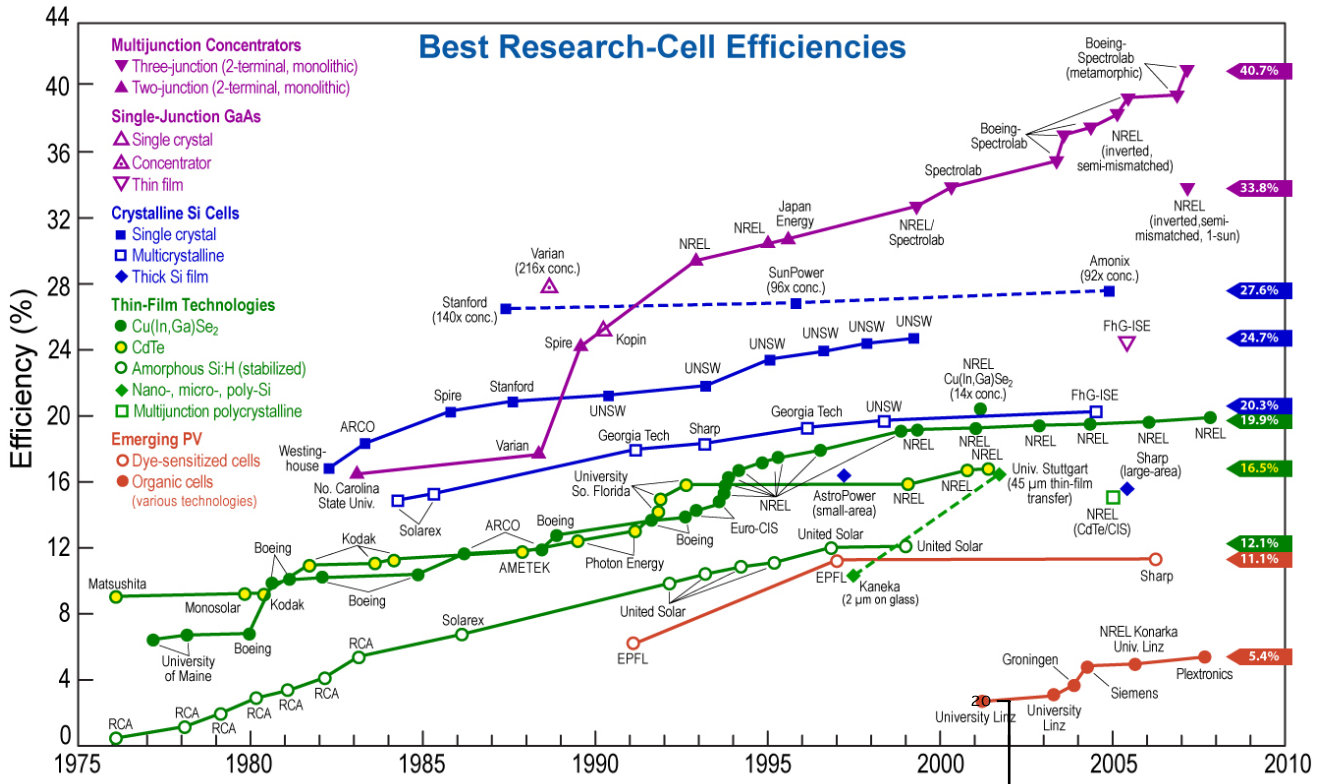
TiO_x optical spacer and stabilizer

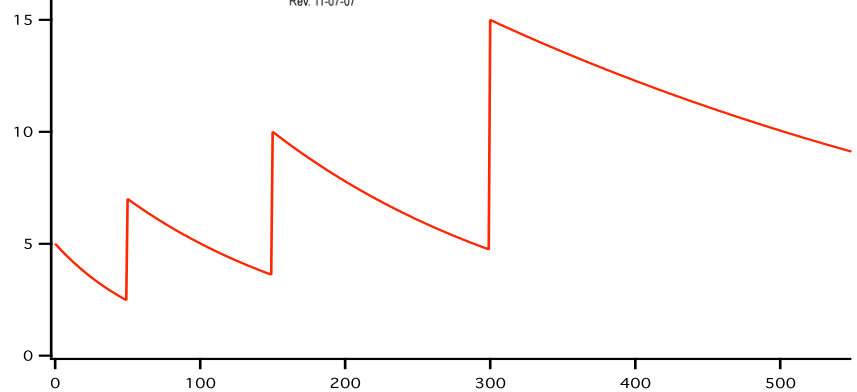




Kim et al., *Adv. Mat.* 18, 572 (2006)

A path forward?





Summary

- Increase efficiencies incrementally for P3HT:PCBM up to a limit of ~7%.
- Provides a foundation on to which new concepts can be tested.
- Learn how bulk heterojunction works. Understand role of interface states.
- Test new electrodes.
- Test new acceptors. (Remember unique property of C_{60}).

- Chemistry is the tool to pave the way forward.
- New red absorbers with more tolerance to attack by oxygen/ water.
- Gain a fundamental understanding of how devices work.
- Foundation for third-generation concepts.

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